

Elementary Theory of Line Broadening and Four-wave Mixing in Nonequilibrium Many-Particle Systems

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Abstract. The basic results of optical line broadening and four-wave mixing are deduced from first principles based on time-dependent many-body perturbation theory. The formalism allows us to write all the results in terms of nonequilibrium distribution functions without the need to assume a quasiequilibrium temperature. The connection of these results to the quantum Boltzmann equation is shown, which is also derived from first principles. Last, specific predictions for electron-electron scattering are reviewed.

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There are many optical experiments which measure linewidths, lifetimes, T_1 times and T_2 times, etc., but it is not always clear how these relate to each other in terms of the basic quantum mechanics. This paper gives a basic introduction to these experiments based on elementary time-dependent many-body perturbation theory in the random-phase approximation. Of primary interest is to be able to write down this theory for the general case of a nonequilibrium many-body system without assuming an equilibrium temperature. We do not want even to assume a perturbation around a quasiequilibrium system, but a system which is far from equilibrium, e.g. a shell in momentum space. This type of highly nonequilibrium system is often created in ultrafast laser experiments.

It turns out that it is nontrivial to show a very basic experimental result, that optical lines are broadened in the shape of a Lorentzian which has width proportional to the instantaneous scattering rate, in the case of a nonequilibrium many-body system. The assumptions necessary to deduce this result in turn show the limits of its applicability.

1 Time-Dependent Perturbation Theory

The theory here is based on standard time-dependent perturbation theory, e.g. as presented by Baym [1]. We review here the basic results given in Chapter 12 of Baym.

We begin by assuming that the Hamiltonian of a quantum mechanical system is given by

$$H = H_0 + V,$$

where H_0 is the single-particle Hamiltonian and V is a scattering term which is small compared to H_0 . The system of interest can be anything from free atoms or ions to carriers in a semiconductor or metal. We ignore all relativistic effects, however.

We assume that the system has been prepared at time $t = 0$ in the quantum mechanical state $|\psi_0\rangle$. At a later time t , the state is written as $|\psi_t\rangle$.

The Schrödinger equation gives the time evolution of the system as

$$i\hbar \frac{\partial}{\partial t} |\psi_t\rangle = (H_0 + V) |\psi_t\rangle$$

In the interaction representation, we define a new state $|\psi(t)\rangle$ (t in parenthesis rather than subscript) given by

$$|\psi(t)\rangle = e^{iH_0 t/\hbar} |\psi_t\rangle$$

and a new operator $V(t) = e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}$. In this representation, the Schrödinger equation is rewritten as

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = V(t) |\psi(t)\rangle,$$

which has the advantage of not depending on H_0 .

Integrating this equation as a perturbation series, one can show that [1]

$$\begin{aligned} |\psi(t)\rangle &= e^{-(i/\hbar) \int V(t) dt} |\psi(0)\rangle \\ &= \left(1 + (1/i\hbar) \int_0^t V(t') dt' + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' V(t') V(t'') + \dots \right) |\psi(0)\rangle \end{aligned} \tag{1}$$

2 Connection to Time-Independent Perturbation Theory

In general, we are interested in knowing the amount of depletion of the initial state after some time t . Abbreviating $|\psi(0)\rangle = |0\rangle$, we write

$$\begin{aligned}
\langle 0|\psi(t)\rangle &= \left(1 + (1/i\hbar)\langle 0|V|0\rangle \int_0^t dt' \right. \\
&\quad + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' \sum_m \langle 0|V|m\rangle \langle m|V|0\rangle e^{(i/\hbar)(E_0-E_m)t'} e^{(i/\hbar)(E_m-E_0)t''} \\
&\quad + (1/i\hbar)^3 \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' \sum_{m,n} \langle 0|V|n\rangle \langle n|V|m\rangle \langle m|V|0\rangle \\
&\quad \left. \times e^{(i/\hbar)(E_0-E_n)t'} e^{(i/\hbar)(E_n-E_m)t''} e^{(i/\hbar)(E_m-E_0)t'''} + \dots \right). \tag{2}
\end{aligned}$$

Here we have inserted a sum over the complete set of states $\sum |m\rangle\langle m| = 1$ which are assumed to be eigenstates of the Hamiltonian H_0 . Then we have

$$\begin{aligned}
\langle 0|\psi(t)\rangle &= \left(1 + (1/i\hbar)t\langle 0|V|0\rangle + \frac{1}{2}(1/i\hbar)^2 t^2 |\langle 0|V|0\rangle|^2 \right. \\
&\quad + (1/i\hbar) \sum_{m \neq 0} \int_0^t dt' \frac{|\langle m|V|0\rangle|^2}{E_0 - E_m + i\eta} e^{(i/\hbar)(E_0-E_m)t'} \left(e^{(i/\hbar)(E_m-E_0)t'} - 1 \right) \\
&\quad + \frac{1}{3!}(1/i\hbar)^3 t^3 |\langle 0|V|0\rangle|^3 \\
&\quad + 2(1/i\hbar)^2 \langle 0|V|0\rangle \sum_{m \neq 0} \int_0^t dt' \int_0^{t'} dt'' \frac{|\langle m|V|0\rangle|^2}{E_0 - E_m + i\eta} e^{(i/\hbar)(E_0-E_m)t'} \\
&\quad \left. \times \left(e^{(i/\hbar)(E_m-E_0)t'} - 1 \right) + \dots \right). \tag{3}
\end{aligned}$$

In going from (2) to (3), we have used some assumptions. The upper and lower bounds of each time integral give terms of the form

$$\left(e^{(i/\hbar)(E_m-E_0)t'} - 1 \right).$$

The first, exponential term cancels the exponential term of the next time integral. The second term, -1, gives a vanishing term in the integration because when the last time integration over dt' is performed, it gives an integral of the form

$$\int \mathcal{D}(E_m) dE_m \left(e^{i(E_m-E_0)t/\hbar} - 1 \right) \frac{|\langle m|V|0\rangle|^2}{(E_0 - E_m)^2}.$$

Assuming $\mathcal{D}(E_m)|\langle m|V|0\rangle|^2$ is continuous and slowly varying with E_m , this integral vanishes because the leading term is odd, i.e.

$$\left(e^{i(E_m-E_0)t/\hbar} - 1 \right) \simeq i(E_m - E_0)t/\hbar$$

for $(E_m - E_0) \simeq 0$, and when $(E_m - E_0) \gg 0$, the $1/(E_0 - E_m)^2$ term in the denominator and the fast oscillation of the $e^{i(E_m - E_0)t/\hbar}$ term kill this integral. This is the “random-phase approximation” (RPA); essentially, it means that we ignore memory of the past and keep only terms from the upper bound of the time integrals.

Note also that rigorously, to introduce the term $i\eta$ in the denominator, which allows us to treat the pole at $E_m = E_0$, we must assume that $V = V e^{-\eta t}$, where $\eta \rightarrow 0$. Then we will have

$$\int_0^t e^{-\eta t'} dt' = \frac{e^{-\eta t} - 1}{-\eta} = \frac{1 - \eta t + \dots - 1}{-\eta} = t$$

and

$$\begin{aligned} \int_0^t \int_0^{t'} e^{-\eta t'} e^{-\eta t''} dt' dt'' &= \int_0^t e^{-\eta t'} \frac{e^{-\eta t'} - 1}{-\eta} dt' = \frac{e^{-2\eta t} - 1}{2\eta^2} - \frac{e^{-\eta t} - 1}{\eta^2} \\ &= \frac{(1 - 2\eta t + 2\eta^2 t^2 + \dots - 1) - 2(1 - \eta t + \frac{1}{2}t^2 + \dots - 1)}{2\eta^2} = \frac{1}{2}t^2, \end{aligned}$$

etc., which gives us the same result as if we had simply done the integrals assuming V is time-independent and then inserted $i\eta$ wherever it is needed to take care of a pole.

The series in (3) has the same form as the series expansion of an exponential. By induction, we can write

$$\langle 0|\psi(t)\rangle = \exp \left[-(i/\hbar) \left(\langle 0|V|0\rangle + \sum_{m \neq 0} \frac{|\langle m|V|0\rangle|^2}{E_0 - E_m + i\eta} + \dots \right) t \right] \quad (4)$$

This result (4) is extremely useful. It is not an approximation, but is exact to all orders of t , within the limits of the RPA, for any time-independent V . The series inside the exponential is just the time-independent perturbation series for the energy correction due to the particle interactions (see, e.g. Baym [1], chapter 11), which is typically called “Rayleigh-Schrödinger” perturbation theory.

By the Dirac formula, the second-order term is

$$\begin{aligned} \sum_{m \neq 0} \frac{|\langle m|V|0\rangle|^2}{E_0 - E_m + i\eta} &= P \left(\sum_{m \neq 0} \frac{|\langle m|V|0\rangle|^2}{E_0 - E_m} \right) - i\pi \sum_{m \neq 0} |\langle m|V|0\rangle|^2 \delta(E_0 - E_m) \\ &= \Delta^{(2)} - i\Gamma^{(2)} \end{aligned} \quad (5)$$

where the second term is just the total scattering rate. $\Delta^{(1)} = \langle 0|V|0\rangle$ is called the mean-field energy, $\Delta^{(2)}$ is called the real self-energy and $\Gamma^{(2)}$ is called the imaginary self-energy. From (4) we have therefore

$$\langle 0|\psi(t)\rangle = e^{-(i/\hbar)(\Delta^{(1)} + \Delta^{(2)} - i\Gamma^{(2)})t} \quad (6)$$

The probability of being in the state $|0\rangle$, given by $|\langle 0|\psi(t)\rangle|^2$, decreases over time as $e^{-(2\Gamma/\hbar)t}$ due to out-scattering. Thus one can see the reason why the imaginary self-energy is associated with an out-scattering rate.

3 Absorption and Emission Line Shape in the Single-Particle Picture

We now imagine that we have a single particle prepared in a given state which can decay by two channels, namely by coupling to an external field (normally a photon field) and by scattering to other internal states. We write

$$H = H_0 + V + V'$$

where V' is a smaller perturbation than V , which gives the interband photon-electron interaction. We will only be concerned about the first-order contributions of this term, i.e. we will not worry about renormalization of the electron states due to electron-photon interaction. We will allow renormalization due to V , however. Therefore we write

$$|\psi'(t)\rangle = |\psi(0)\rangle + \frac{1}{i\hbar} \int_0^t dt' V'(t') |\psi(t')\rangle,$$

where $|\psi(t')\rangle$ is assumed to include the evolution due to V given in (1).

We are interested in the rate of emission of a photon with frequency ω and momentum \mathbf{k} . We assume that the eigenstates of H_0 are single-particle states, each with a given momentum. Therefore by momentum conservation, only one state with momentum \mathbf{k} , which we will identify as $|0\rangle$, couples to the photon state $|\omega, \mathbf{k}\rangle$. We write the rate of emission as the probability of being in the photon state $|\omega, \mathbf{k}\rangle$ at $t = \infty$, after starting in the initial state $|0\rangle$, divided by the total time spent in the initial state:

$$\frac{1}{\tau(\omega, \mathbf{k})} = \frac{|\langle\omega, \mathbf{k}|\psi'(\infty)\rangle|^2}{\int_0^\infty dt |\langle 0|\psi(t)\rangle|^2}.$$

By the assumptions above, by momentum conservation we write $\langle\omega, \mathbf{k}|V'|m\rangle = \langle V'\rangle\delta_{0,m}$. Then we have

$$\begin{aligned} |\langle\omega, \mathbf{k}|\psi'(\infty)\rangle|^2 &= \left| \frac{1}{i\hbar} \int_0^\infty dt' \sum_m \langle\omega, \mathbf{k}|e^{(i/\hbar)H_0 t'} V' e^{-(i/\hbar)H_0 t'} |m\rangle \langle m|\psi(t')\rangle \right|^2 \\ &= \left| \frac{1}{i\hbar} \int_0^\infty dt' \langle\omega, \mathbf{k}|V'|0\rangle e^{i\omega t'} e^{-(i/\hbar)E_0 t'} \langle 0|\psi(t')\rangle \right|^2 \\ &= |\langle V'\rangle|^2 \left| \frac{1}{i\hbar} \int_0^\infty dt e^{i\omega t} e^{-(i/\hbar)E_0 t} e^{-(i/\hbar)(\Delta^{(1)} + \Delta^{(2)} - i\Gamma^{(2)})t} \right|^2 \\ &= |\langle V'\rangle|^2 \left| \frac{1}{\hbar\omega - E - i\Gamma} \right|^2 \\ &= |\langle V'\rangle|^2 \frac{1}{(\hbar\omega - E)^2 + \Gamma^2} \end{aligned}$$

where we have abbreviated $E = E_0 + \Delta^{(1)} + \Delta^{(2)}$ and $\Gamma = \Gamma^{(2)}$ from (6). The normalization factor is

$$\begin{aligned} \int_0^\infty dt |\langle 0|\psi(t)\rangle|^2 &= \int_0^\infty dt \left| e^{-(i/\hbar)(\Delta^{(1)} + \Delta^{(2)} - i\Gamma^{(2)})t} \right|^2 \\ &= \int_0^\infty dt e^{-2\Gamma t/\hbar} \\ &= \frac{\hbar}{2\Gamma} \end{aligned}$$

This gives the total rate as

$$\frac{1}{\tau(\omega, \mathbf{k})} = |\langle V' \rangle|^2 \frac{2\Gamma/\hbar}{(\hbar\omega - E)^2 + \Gamma^2} \quad (7)$$

which when $\Gamma \rightarrow 0$, is

$$\frac{1}{\tau(\omega, \mathbf{k})} = \frac{2\pi}{\hbar} |\langle V' \rangle|^2 \delta(\hbar\omega - E).$$

The interpretation of this result is that while the photon has definite momentum and energy, the particle emitting the photon has definite momentum but indefinite energy. The energy uncertainty comes from the Heisenberg uncertainty relation $\Delta E \Delta t \geq \hbar$, that is, the shorter the time spent in state $|0\rangle$, the greater the energy uncertainty.

4 Connection to the Boltzmann Equation in Many-Particle Theory

We have so far been vague about the nature of the interaction V . In the previous section we assumed that we had a set of single-particle states with a time-independent out-scattering term V . In general, however, the particle of interest will be one of many particles in a system, and V will be an interaction term between the particles.

The theory of Sections 1 and 2 is completely general; that is, the state $|0\rangle$ can be taken as a many-particle state instead of a single-particle state. If it is taken as a many-particle state, however, then the result (6) is not as useful, since it involves the total self-energy of the system, while we are typically interested in the single-particle self-energy.

We define the instantaneous many-particle state using creation and destruction operators $a_{\mathbf{k}}$ and $a_{\mathbf{k}}^\dagger$ (Baym [1], chapter 19) as

$$|0\rangle = \prod_{\mathbf{k}} \frac{(a_{\mathbf{k}}^\dagger)^{n_{\mathbf{k}}}}{\sqrt{n_{\mathbf{k}}!}} |\text{vac}\rangle, \quad (8)$$

where $n_{\mathbf{k}}$ gives the instantaneous occupation number of each state (this is called a “Fock” state). The “vacuum” state $|\text{vac}\rangle$ is the zero-particle state, which in the case of a solid means the ground state of the system. Note that we do not need to assume an *equilibrium* distribution of particles; we can use an instantaneous nonequilibrium distribution if we have that information.

A typical interaction term is written in terms of the same creation and destruction operators, e.g. a two-body, number-conserving term,

$$V = \frac{1}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3} U_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \quad (9)$$

where the summation is not over \mathbf{k}_4 because it is implicitly assumed that momentum is conserved so that $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$. The interaction energy U is assumed to be symmetric on exchange of \mathbf{k}_1 with \mathbf{k}_3 or \mathbf{k}_2 with \mathbf{k}_4 .

We are concerned about the evolution of the single-particle state \mathbf{k} , which is to say, the number of particles in state \mathbf{k} as a function of time. The change in the number of particles in a time t is given by

$$d\langle n_{\mathbf{k}} \rangle = \langle \psi_t | n_{\mathbf{k}} | \psi_t \rangle - \langle 0 | n_{\mathbf{k}} | 0 \rangle$$

$$\begin{aligned}
&= \langle \psi(t) | e^{iH_0 t/\hbar} n_{\mathbf{k}} e^{-iH_0 t/\hbar} | \psi(t) \rangle - \langle 0 | n_{\mathbf{k}} | 0 \rangle \\
&= \langle 0 | e^{(i/\hbar) \int V(t) dt} n_{\mathbf{k}} e^{-(i/\hbar) \int V(t) dt} | 0 \rangle - \langle 0 | n_{\mathbf{k}} | 0 \rangle \\
&= \langle 0 | e^{(i/\hbar) \int V(t) dt} [n_{\mathbf{k}}, e^{-(i/\hbar) \int V(t) dt}] | 0 \rangle.
\end{aligned} \tag{10}$$

The operator $n_{\mathbf{k}}$ commutes with H_0 , by definition. If it commutes with V , then there is no change in $\langle n_{\mathbf{k}} \rangle$ over time. We can resolve the commutator in (10) by using the relations

$$\begin{aligned}
[n_{\mathbf{k}}, a_{\mathbf{k}'}] &= -a_{\mathbf{k}} \delta_{\mathbf{k}, \mathbf{k}'} \\
[n_{\mathbf{k}}, a_{\mathbf{k}'}^\dagger] &= a_{\mathbf{k}}^\dagger \delta_{\mathbf{k}, \mathbf{k}'}
\end{aligned} \tag{11}$$

which are valid, surprisingly, for both boson and fermion creation and destruction operators. For a four-operator term in the interaction (9), we have

$$\begin{aligned}
n_{\mathbf{k}} a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} &= a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \delta_{\mathbf{k}, \mathbf{k}_4} + a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \delta_{\mathbf{k}, \mathbf{k}_3} \\
&\quad - a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \delta_{\mathbf{k}, \mathbf{k}_2} - a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \delta_{\mathbf{k}, \mathbf{k}_1} \\
&\quad + a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} n_{\mathbf{k}}
\end{aligned}$$

Thus

$$\begin{aligned}
[n_{\mathbf{k}}, V] &= \frac{1}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \left(U_{0321} a_{\mathbf{k}}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} + U_{3021} a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} - U_{3201} a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}} a_{\mathbf{k}_1} - U_{3210} a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1} a_{\mathbf{k}} \right) \\
&= \frac{1}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2} (U_D \pm U_E) \left(a_{\mathbf{k}}^\dagger a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_3} - a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1} a_{\mathbf{k}} \right)
\end{aligned} \tag{12}$$

where U_D refers to the direct term and U_E to the exchange term, and the $+$ sign is for bosons and the $-$ sign is for fermions. (For hard-sphere scattering, i.e. s-wave scattering, U is a constant, which gives a factor of 4 enhancement of the scattering cross section for bosons and is forbidden for fermions.)

We first write out the series expansion,

$$\begin{aligned}
d\langle n_{\mathbf{k}} \rangle &= \langle 0 | \left(1 - (1/i\hbar) \int_0^t V(t') dt' + \dots \right) \\
&\quad \times \left((1/i\hbar) \int_0^t dt' [n_{\mathbf{k}}, V(t')] + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' [n_{\mathbf{k}}, V(t') V(t'')] + \dots \right) | 0 \rangle
\end{aligned}$$

Any terms in the right-hand series multiplied by the leading “1” in the left-hand series vanish, since $\langle 0 | [n_{\mathbf{k}}, A] | 0 \rangle$ vanishes for any operator A . Note that $V^\dagger(t) = V(t)$. The leading-order term is therefore

$$\begin{aligned}
d\langle n_{\mathbf{k}} \rangle &= \langle 0 | (1/\hbar^2) \left(\int_0^t dt' V(t') \right) \left(\int_0^t dt'' [n_{\mathbf{k}}, V(t'')] \right) | 0 \rangle \\
&= \sum_m (1/\hbar^2) \left(\int_0^t dt' e^{(i/\hbar)(E_0 - E_m)t'} \right) \left(\int_0^t dt'' e^{(i/\hbar)(E_m - E_0)t''} \right) \langle 0 | V | m \rangle \langle m | [n_{\mathbf{k}}, V] | 0 \rangle \\
&= \sum_m \left(\frac{e^{(i/\hbar)(E_0 - E_m)t} - 1}{E_0 - E_m} \right) \left(\frac{e^{-(i/\hbar)(E_0 - E_m)t} - 1}{E_0 - E_m} \right) \langle 0 | V | m \rangle \langle m | [n_{\mathbf{k}}, V] | 0 \rangle
\end{aligned}$$

where the sum over states m is over all possible Fock states. The time-dependent factors are resolved using the identities

$$\begin{aligned}\lim_{t \rightarrow \infty} \frac{(e^{ixt} - 1)(e^{-ixt} - 1)}{x^2} &= \lim_{t \rightarrow \infty} \frac{\sin^2(xt/2)}{x^2} \\ &= \delta(x)2\pi t\end{aligned}$$

We therefore have

$$d\langle n_{\mathbf{k}} \rangle = \sum_m \langle 0|V|m \rangle \langle m|[n_{\mathbf{k}}, V]|0 \rangle \frac{2\pi t}{\hbar} \delta(E_0 - E_m). \quad (13)$$

Since the different Fock states are assumed orthonormal, the summation in V is eliminated because only the terms which couple $|0\rangle$ to $|m\rangle$ survive. Since a destruction operator $a_{\mathbf{k}}$ acting to the right on a state with $n_{\mathbf{k}}$ particles gives a factor $\sqrt{n_{\mathbf{k}}}$, and a creation operator $a_{\mathbf{k}}^\dagger$ gives a factor $\sqrt{1 \pm n_{\mathbf{k}}}$, where the $+$ sign is for bosons (stimulated emission) and the $-$ sign is for fermions (Pauli exclusion), using (12), (13) therefore becomes

$$\begin{aligned}\frac{d\langle n_{\mathbf{k}} \rangle}{dt} &= \frac{2\pi}{\hbar} \sum_{\mathbf{k}_1, \mathbf{k}_2} |U_D \pm U_E|^2 [n_{\mathbf{k}_3} n_{\mathbf{k}_2} (1 \pm n_{\mathbf{k}_1})(1 \pm n_{\mathbf{k}}) - n_{\mathbf{k}} n_{\mathbf{k}_1} (1 \pm n_{\mathbf{k}_2})(1 \pm n_{\mathbf{k}_3})] \\ &\quad \times \delta(E_{\mathbf{k}} + E_{\mathbf{k}_1} - E_{\mathbf{k}_3} - E_{\mathbf{k}_2})\end{aligned} \quad (14)$$

where we have assumed t is a very small quantity dt . This is the quantum Boltzmann equation, which gives the total rate of out-scattering for a state \mathbf{k} . It is the same energy we would have written down if we had simply written the total scattering rate as the sum of the Fermi's Golden Rule rate,

$$\frac{2\pi}{\hbar} |\langle m|V|0 \rangle|^2 \delta(E_0 - E_m),$$

over all allowed processes of single-particle states $|m\rangle$. It is correct to order V^2 , but the limit $t \rightarrow \infty$ in (13) implies that the time step dt must be long compared to the oscillation time $\hbar/(E_0 - E_m)$, i.e. we are not concerned about behavior on time scales so short that the equivalent energy uncertainty is comparable to the typical collision energies. This is the random-phase approximation again.

We can make one simplification of the Boltzmann equation by treating $n_{\mathbf{k}}$ as a continuous variable, in which $n_{\mathbf{k}}$ is equal to its average value in an element of phase space d^3k , and converting the summation to an integral, to get

$$\begin{aligned}\frac{d\langle \bar{n}_{\mathbf{k}} \rangle}{dt} &= \frac{2\pi}{\hbar} \left(\frac{L^3}{(2\pi)^3} \right)^2 \int d^3k_1 d^3k_2 |U_D \pm U_E|^2 [n_{\mathbf{k}_3} n_{\mathbf{k}_2} (1 \pm n_{\mathbf{k}_1})(1 \pm n_{\mathbf{k}}) - n_{\mathbf{k}} n_{\mathbf{k}_1} (1 \pm n_{\mathbf{k}_2})(1 \pm n_{\mathbf{k}_3})] \\ &\quad \times \delta(E_{\mathbf{k}} + E_{\mathbf{k}_1} - E_{\mathbf{k}_3} - E_{\mathbf{k}_2}).\end{aligned} \quad (15)$$

We can make an additional simplification if we assume that the system is *isotropic*, i.e. the distribution function $n_{\mathbf{k}}$ depends only on the magnitude of \mathbf{k} and not on the direction. Then we can integrate analytically over all the angles to reduce this integral to just a double integral which can then be solved numerically for nonequilibrium isotropic distributions. This has been used to produce predictions for various nonequilibrium systems [2, 3, 4, 5].

These different rates clarify the difference between T_1 , T_2 etc. in experiments. The rate (14) gives the rate of depletion of a single quantum state, sometimes called the “dephasing” rate in optics. The time constant

for this decay is called “ T_2 ” in NMR terminology. The rate (15) gives the rate of depletion of states with the same macroscopic characteristics as state \mathbf{k} , and the time constant is called “ T_1 ” in NMR terminology.

We now have calculated the many-body equivalent of the formula (6) for the decay rate. We can now use this in the calculation of line broadening.

5 Line broadening in Many-Particle theory

As in Section 3, we are interested in the rate of emission of a photon with momentum \mathbf{k} and frequency ω from a given initial state, via a weak particle-photon interaction in the presence of a particle-particle interaction. In the many-particle theory we will define the creation and destruction operators $c_{\mathbf{k}}^\dagger$ and $c_{\mathbf{k}}$ for photons; the total many-particle state is a product of Fock states of both photons and the interacting particles. As before, we write $H = H_0 + V + V'$, where V' is the particle-photon interaction term, which we assume has the form

$$V' = \sum_{\mathbf{k}_1} P_{\mathbf{k}_1} c_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_1}.$$

Although this form is strictly unphysical, it is a good model for radiative transitions. Electrons are, of course, conserved, but if we restrict our attention to only one band, then radiative transitions which cause band-to-band transitions involve the destruction of an electron in one band. On the other hand, excitons are not conserved, so this notation allows us to treat electrons and excitons on equal footing as in the previous section. Also, we drop the hermitian conjugate term because we neglect the possibility of photon absorption; we assume there are no photons at $t = 0$.

The number of photons emitted in a time t is then

$$\begin{aligned} \langle N_{\mathbf{k}} \rangle &= \langle \psi(t) | c_{\mathbf{k}}^\dagger c_{\mathbf{k}} | \psi(t) \rangle \\ &= \langle 0 | e^{(i/\hbar) \int (V(t) + V'^\dagger(t)) dt} [c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, e^{-(i/\hbar) \int (V(t) + V'(t)) dt}] | 0 \rangle \end{aligned} \quad (16)$$

As in the previous section, we assume $|0\rangle$ is an exact Fock state which is not an eigenstate of the Hamiltonian. This will complicate the analysis (preventing us from using standard many-body formalism) but allows us to treat the case of a highly nonequilibrium system. As before, we write out the series,

$$\begin{aligned} \langle N_{\mathbf{k}} \rangle &= \langle 0 | \left(1 - (1/i\hbar) \int_0^t (V(t') + V'^\dagger(t')) dt' \right. \\ &\quad \left. + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' (V(t'') + V'^\dagger(t'')) (V(t') + V'^\dagger(t')) \dots \right) \\ &\quad \times \left((1/i\hbar) \int_0^t dt' [c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, (V(t') + V'(t'))] \right. \\ &\quad \left. + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' [c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, (V(t') + V'(t')) (V(t'') + V'(t''))] + \dots \right) | 0 \rangle \end{aligned}$$

Since V' is not number-conserving, only terms with products of the pair $V'^\dagger V'$ survive. We restrict ourselves to only terms which are first order in $V'^\dagger V'$. The photon number $c_{\mathbf{k}}^\dagger c_{\mathbf{k}}$ commutes with $V(t)$, while the relation (11) implies that $[c_{\mathbf{k}}^\dagger c_{\mathbf{k}}, V'] = P_{\mathbf{k}} c_{\mathbf{k}}^\dagger a_{\mathbf{k}}$, which in turn implies that only terms with $V'^\dagger = P_{\mathbf{k}}^* a_{\mathbf{k}}^\dagger c_{\mathbf{k}}$ survive.

At this point we can make an additional assumption in order to greatly simplify the calculation. This is to assume the “dilute” limit, which is that the occupation number of state \mathbf{k} in $|0\rangle$ is not greater than one, and in-scattering to any particular state \mathbf{k} is negligible compared to out-scattering. One can see that this will be the case because for any out-scattering term $a_{\mathbf{k}}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1}$ for which the four momenta satisfy momentum conservation exactly, the probability of having both of states \mathbf{k}_1 and \mathbf{k}_2 occupied simultaneously is very low. Note that in equilibrium, the average net scattering into and out of any state over a long time equals zero, but in this case the many-body state $|0\rangle$ has been prepared with $n_{\mathbf{k}} = 1$ at $t = 0$, and therefore the out-scattering *at that time* will greatly exceed the in-scattering.

In terms like VV' there are combinations like $a_{\mathbf{k}_4}^\dagger a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} a_{\mathbf{k}}$. No double occupancy means that terms with $a_{\mathbf{k}} a_{\mathbf{k}}$ vanish. On the other hand, terms in V for which no $\mathbf{k}_i = \mathbf{k}$ commute with $a_{\mathbf{k}}$ and one can show that all such terms vanish. We will use $V_{\mathbf{k}}(t)$ to indicate the subset of terms in the summation of $V(t)$ which do not commute with $a_{\mathbf{k}}$. We then get

$$\begin{aligned}
\langle N_{\mathbf{k}} \rangle &= \langle 0 | P_{\mathbf{k}} |^2 \left(- (1/i\hbar) \int_0^t a_{\mathbf{k}}^\dagger c_{\mathbf{k}} e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' V_{\mathbf{k}}(t'') a_{\mathbf{k}}^\dagger c_{\mathbf{k}} e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} \right. \\
&\quad \left. - (1/i\hbar)^3 \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' V_{\mathbf{k}}(t''') V_{\mathbf{k}}(t'') a_{\mathbf{k}}^\dagger c_{\mathbf{k}} e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} + \dots \right) \\
&\quad \times \left((1/i\hbar) \int_0^t dt' c_{\mathbf{k}}^\dagger a_{\mathbf{k}} e^{(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} + (1/i\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' c_{\mathbf{k}}^\dagger a_{\mathbf{k}} e^{(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} V_{\mathbf{k}}(t'') \right. \\
&\quad \left. + (1/i\hbar)^3 \int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' c_{\mathbf{k}}^\dagger a_{\mathbf{k}} e^{(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} V_{\mathbf{k}}(t'') V_{\mathbf{k}}(t''') + \dots \right) |0\rangle \\
&= |P_{\mathbf{k}}|^2 \langle 0 | \left(- (1/i\hbar) \int_0^t e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' \right) \\
&\quad \times \left(1 - (1/i\hbar) \int_0^{t'} V_{\mathbf{k}}(t'') dt'' + (1/i\hbar)^2 \int_0^{t'} \int_0^{t''} V_{\mathbf{k}}(t'') V_{\mathbf{k}}(t''') dt'' dt''' - \dots \right) \\
&\quad \times n_{\mathbf{k}} \left((1/i\hbar) \int_0^t e^{(1/i\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' \right) \\
&\quad \times \left(1 + (1/i\hbar) \int_0^{t'} V_{\mathbf{k}}(t'') dt'' + (1/i\hbar)^2 \int_0^{t'} \int_0^{t''} V_{\mathbf{k}}(t'') V_{\mathbf{k}}(t''') dt'' dt''' + \dots \right) |0\rangle \\
&= \frac{|P_{\mathbf{k}}|^2}{\hbar^2} \langle 0 | \left(\int_0^t e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' \right) e^{(i/\hbar) \int_0^{t'} V_{\mathbf{k}}(t'') dt''} \\
&\quad \times n_{\mathbf{k}} \left(\int_0^t e^{(1/i\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' \right) e^{-(i/\hbar) \int_0^{t'} V_{\mathbf{k}}(t'') dt''} |0\rangle
\end{aligned} \tag{17}$$

We now break this into two parts, inserting a complete set of states $\sum |m\rangle \langle m|$ and separating the term with $|0\rangle \langle 0|$ from the rest.

$$\langle N_{\mathbf{k}} \rangle = \frac{|P_{\mathbf{k}}|^2}{\hbar^2} \left[\left(\int_0^t e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' \langle 0 | e^{(i/\hbar) \int_0^{t'} V_{\mathbf{k}}(t'') dt''} |0\rangle \right) \right]$$

$$\begin{aligned}
& \times n_{\mathbf{k}} \left(\int_0^t e^{(1/i\hbar)(\hbar\omega - E_{\mathbf{k}})t'} dt' \langle 0 | e^{-(i/\hbar) \int_0^{t'} V_{\mathbf{k}}(t'') dt''} | 0 \rangle \right) \\
& + \sum_{m \neq 0} (1/\hbar^2) \left| \int_0^t dt' e^{-(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} \int_0^{t'} dt'' \langle 0 | V_{\mathbf{k}}(t'') | m \rangle \right|^2 + \dots \Big] \quad (18)
\end{aligned}$$

The second, cross term vanishes, having terms like

$$\left| \int_0^t dt' e^{i\omega_1 t'} \frac{e^{i\omega_2 t'} - 1}{\omega_2} \right|^2 = \left| \frac{e^{i(\omega_1 + \omega_2)t} - 1}{(\omega_1 + \omega_2)\omega_2} - \frac{e^{i\omega_1 t}}{\omega_1\omega_2} \right|^2$$

which vanish in the limit of the random-phase approximation, while the other factors are given by (4) – (6). In the limit $t \rightarrow \infty$, we then have

$$\begin{aligned}
\langle N_{\mathbf{k}} \rangle &= \frac{|P_{\mathbf{k}}|^2}{\hbar^2} \langle n_{\mathbf{k}} \rangle \left| \int_0^\infty dt' e^{(i/\hbar)(\hbar\omega - E_{\mathbf{k}})t'} e^{-(i/\hbar)(\Delta^{(1)} + \Delta^{(2)} - i\Gamma^{(2)})t'} \right|^2 \\
&= |P_{\mathbf{k}}|^2 \langle n_{\mathbf{k}} \rangle \frac{1}{(\hbar\omega - E)^2 + \Gamma^2}, \quad (19)
\end{aligned}$$

where we have used the abbreviated notation for E and Γ of Section 3, and

$$\begin{aligned}
\Gamma^{(2)} &= \pi \sum_{m \neq 0} |\langle m | V_{\mathbf{k}} | 0 \rangle|^2 \delta(E_0 - E_m) \\
&= \pi \sum_{m \neq 0} \left| \langle m | \frac{1}{2} \sum_{\mathbf{k}_1, \mathbf{k}_2} (U_D \pm U_E) a_{\mathbf{k}_3}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_1} a_{\mathbf{k}} | 0 \rangle \right|^2 \delta(E_0 - E_m) \\
&= \pi \sum_{\mathbf{k}_1, \mathbf{k}_2} |U_D \pm U_E|^2 n_{\mathbf{k}} n_{\mathbf{k}_1} (1 \pm n_{\mathbf{k}_2}) (1 \pm n_{\mathbf{k}_3}) \delta(E_{\mathbf{k}} + E_{\mathbf{k}_1} - E_{\mathbf{k}_2} - E_{\mathbf{k}_3}) \quad (20)
\end{aligned}$$

Note that the integral in (20) is the same as in (14), neglecting the in-flow terms, which are negligible in the dilute limit for a *particular* state \mathbf{k} , even though the average in-flow to a region of phase space d^3k around state \mathbf{k} , found in (15), equals the out-flow from the same region in equilibrium.

We can rewrite (19) as

$$\begin{aligned}
\frac{d\langle N_{\mathbf{k}} \rangle}{dt} &= |P_{\mathbf{k}}|^2 \frac{d\langle n_{\mathbf{k}} \rangle}{dt} \frac{1}{(\hbar\omega - E)^2 + \Gamma^2} \\
&= |P_{\mathbf{k}}|^2 \frac{2\Gamma/\hbar}{(\hbar\omega - E)^2 + \Gamma^2} \quad (21)
\end{aligned}$$

in which (14) is used to obtain $d\langle n_{\mathbf{k}} \rangle/dt \equiv -2\Gamma/\hbar$.

This all has been essentially a long justification of a very simple formula, which we already obtained in (7) using the single-particle picture. This calculation shows the limits of validity of this formula, however. In particular, it assumes the dilute limit. In the gas of a high-density boson gas, the situation is much more complex, as shown by Shi, Verachaka and Griffin [6] for case of a quasiequilibrium boson gas. When state \mathbf{k} is nondegenerate, however, this calculation shows that we can use the the interaction

term $V' = \sum |U_D \pm U_E| \sqrt{n_1} \sqrt{1 \pm n_2} \sqrt{1 \pm n_3}$ with generality in the single-particle picture for a particle in interacting with a bath that is in equilibrium or far from equilibrium. This type of interaction potential has been used to predict the Lorentzian line broadening of luminescence from various semiconductors [7, 8], known as “homogeneous” broadening (as opposed to “inhomogeneous” broadening, due to random fluctuations of the band gap.)

An even simpler method, which is justified by this calculation, is to simply write $H = H'_0 + V'$ where H'_0 includes the self-energy correction to the single-particle energy due to scattering by V . In this case we would write $e^{(i/\hbar)H'_0 t}|0\rangle = e^{(i/\hbar)(E_{\mathbf{k}} + \Delta_{\mathbf{k}}^{(1)} + \Delta_{\mathbf{k}}^{(2)} - i\Gamma^{(2)})t}$ and then treat the interaction V' in first-order perturbation theory.

An important implication of the calculations here is that even in the case when there is substantial line broadening, the energy conserving delta-function in (14) should *not* be replaced by a Lorentzian. One can show that if one were to do this, total energy conservation of the system would be violated.

6 The Connection to $\chi^{(3)}$ in Four-Wave Mixing

We have seen that the imaginary self energy gives the line broadening of optical transitions. Alternatively, as seen above, it also corresponds to the out-scattering rate. This rate can often be measured directly in time-resolved measurements. The two methods are complementary. If the rate is extremely fast, it may be too fast for time-resolved methods, but then it gives significant line broadening. On the other hand, if the line broadening is too small for the experimental spectral resolution to pick up, it corresponds to slow decay rate in time-resolved measurements.

The nonlinear susceptibility is defined in terms of Maxwell’s wave equation in the presence of a polarization current J ,

$$\frac{\partial^2 E}{\partial x^2} = \mu_0 \epsilon_0 \frac{\partial^2 E}{\partial t^2} + \mu_0 \frac{\partial J}{\partial t}. \quad (22)$$

The polarization current depends on the electric field in a complex way, which is represented to third order as

$$J = \epsilon_0 \frac{\partial}{\partial t} \left(\chi E + \chi^{(2)} E^2 + \chi^{(3)} E^3 \right). \quad (23)$$

To calculate $\chi^{(3)}$ from first principles, then, we need to calculate the current due to the oscillating dipole moment of the medium. If we recall that the $\mathbf{J} = e\mathbf{V} = e\mathbf{P}/m$, we see that fundamentally we want to calculate the momentum $\langle P \rangle$ of the oscillator as a function of electric field. The value of $\chi^{(3)}$ can then be identified as the part of this which depends to the third order on the electric field E .

For simplicity we will assume that the oscillator has two states which couple only weakly to other states. These two states nominally correspond to the valence and conduction electron bands in a semiconductor. We will label the ground state $|v\rangle$ and the excited state $|c\rangle$. We will also assume that the light field couples only the valence band to the excited band and has no effect on coupling within bands.

Having justified its use in the previous section, we use the simple approach of replacing each state’s energy with the appropriate renormalized energy including imaginary self-energy due to intraband interactions, subject to the same constraint of no multiple occupancy of states, and treat the optical transitions in first-order perturbation theory. Let the time-dependent electron state be $|e_t\rangle$. In the interaction representation we use $|e(t)\rangle = e^{iH_0 t/\hbar} |e_t\rangle$. Then the oscillator momentum of interest is

$$P(t) = \langle e_t | P | e_t \rangle = \langle e(t) | e^{iH_0 t/\hbar} P e^{-iH_0 t/\hbar} | e(t) \rangle \quad (24)$$

$$\begin{aligned}
&= \langle e(t) | e^{iH_0 t/\hbar} \sum_i |i\rangle \langle i| P \sum_j |j\rangle \langle j| e^{-iH_0 t/\hbar} |e(t)\rangle \\
&= \langle e(t) | c \rangle e^{i(E_c + i\Gamma_c)t/\hbar} \langle c | P | v \rangle \langle v | e(t) \rangle e^{-i(E_v - i\Gamma_v)t/\hbar} \\
&\quad + \langle e(t) | v \rangle e^{i(E_v + i\Gamma_v)t/\hbar} \langle v | P | c \rangle \langle c | e(t) \rangle e^{-i(E_c - i\Gamma_c)t/\hbar} \\
&= 2\Re \langle v | P | c \rangle \langle e(t) | v \rangle \langle c | e(t) \rangle e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar},
\end{aligned}$$

where $\langle v | P | c \rangle$ is the standard oscillator strength of the transition.

The time dependence of the electronic state in response to the electric field is determined by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |e_t\rangle = H |e_t\rangle \quad (25)$$

$$H = H_0 + V' \quad (26)$$

$$V' = \frac{e}{2mc} P \cdot A \quad (27)$$

$$E = -\frac{1}{c} \frac{\partial A}{\partial t}. \quad (28)$$

V' is the radiation term which connects the valence and conduction band states, and H_0 is the total Hamiltonian of the electron states. A and E are assumed to be classical fields. Let $A(t) = A_0 e^{-i\omega t}$. Then

$$E(t) = (i/c) A_0 \omega e^{-i\omega t} = E_0 e^{-i\omega t} \quad (29)$$

which implies

$$V' = \frac{eP \cdot E_0}{2m\omega} e^{-i\omega t} \quad (30)$$

In the interaction representation,

$$V'(t) = e^{iH_0 t/\hbar} \frac{ePE_0}{2m\omega} e^{-i\omega t} e^{-iH_0 t/\hbar}. \quad (31)$$

Third-order time-dependent perturbation theory then gives

$$\begin{aligned}
|e(t)\rangle &= |e(t_0)\rangle + \frac{1}{i\hbar} \int_{t_0}^t dt' V'(t') |e(t_0)\rangle \\
&\quad + \frac{1}{(i\hbar)^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' V'(t') V'(t'') |e(t_0)\rangle \\
&\quad + \frac{1}{(i\hbar)^3} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' V'(t') V'(t'') V'(t''') |e(t_0)\rangle
\end{aligned} \quad (32)$$

where $t_0 \rightarrow -\infty$.

Let $|e(t_0)\rangle = |v\rangle$. Then since we assume that V' does not couple intraband states, so that only $\langle c | V' | v \rangle$ terms survive, we have

$$\langle c | e(t) \rangle = \frac{1}{i\hbar} \int_{t_0}^t dt' \langle c | V'(t') | v \rangle \quad (33)$$

$$\begin{aligned}
& + \frac{1}{(i\hbar)^3} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' \langle c|V'(t')|v \rangle \langle v|V'(t'')|c \rangle \langle c|V'(t''')|v \rangle \\
\langle v|e(t) \rangle & = 1 + \frac{1}{(i\hbar)^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \langle v|V'(t')|c \rangle \langle c|V'(t'')|v \rangle
\end{aligned}$$

Therefore

$$\begin{aligned}
P(t) & = 2\Re \langle v|P|c \rangle e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar} \left[\frac{1}{i\hbar} \int_{t_0}^t dt' \langle c|V'(t')|v \rangle \right. \\
& + \frac{1}{(i\hbar)^3} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' \langle c|V'(t')|v \rangle \langle v|V'(t'')|c \rangle \langle c|V'(t''')|v \rangle \\
& + \frac{1}{(i\hbar)^3} \left(\int_{t_0}^t dt' \langle c|V'(t')|v \rangle \right) \left(\int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \langle c|V'(t')|v \rangle \langle v|V'(t'')|c \rangle \right) \\
& \left. + \mathcal{O}(V'^5) \right]
\end{aligned} \tag{34}$$

There is no second-order $\chi^{(2)}$ by symmetry. We will concentrate on the first third-order term; the calculation of the second term gives similar results.

Substituting in for $V'(t)$, and performing the time integrals explicitly, we get

$$\begin{aligned}
P(t) & = 2\Re \left[|\langle v|P|c \rangle|^2 e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar} \frac{eE_0}{2m\omega} \frac{1}{i\hbar} \int_{t_0}^t dt' e^{i(E_c - i\Gamma_c)t'/\hbar} e^{-i\omega t'} e^{-i(E_v + i\Gamma_v)t'/\hbar} \right. \\
& + |\langle v|P|c \rangle|^4 e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar} \left(\frac{eE_0}{2m\omega} \right)^3 \frac{1}{(i\hbar)^3} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt''' \\
& \times \left(e^{i(E_c - i\Gamma_c)t'/\hbar} e^{-i\omega t'} e^{-i(E_v + i\Gamma_v)t'/\hbar} \right) \left(e^{i(E_v - i\Gamma_v)t''/\hbar} e^{-i\omega t''} e^{-i(E_c + i\Gamma_c)t''/\hbar} \right) \\
& \times \left. \left(e^{i(E_c - i\Gamma_c)t'''/\hbar} e^{-i\omega t'''} e^{-i(E_v + i\Gamma_v)t'''/\hbar} \right) \right]
\end{aligned} \tag{35}$$

$$\begin{aligned}
& = 2\Re \left[|\langle v|P|c \rangle|^2 e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar} \frac{eE_0}{2m\omega} \frac{e^{i(E_c - \hbar\omega - E_v)t/\hbar}}{(E_c - E_v - \hbar\omega + i(\Gamma_c + \Gamma_v))} e^{(\Gamma_v + \Gamma_c)t/\hbar} \right. \\
& + |\langle v|P|c \rangle|^4 e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar} \left(\frac{eE_0}{2m\omega} \right)^3 \frac{1}{(i\hbar)^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \\
& \times \left(e^{i(E_c - i\Gamma_c)t'/\hbar} e^{-i\omega t'} e^{-i(E_v + i\Gamma_v)t'/\hbar} \right) \left(e^{i(E_v - i\Gamma_v)t''/\hbar} e^{-i\omega t''} e^{-i(E_c + i\Gamma_c)t''/\hbar} \right) \\
& \times \frac{e^{i(E_c - \hbar\omega - E_v)t''/\hbar}}{(E_c - E_v - \hbar\omega + i(\Gamma_c + \Gamma_v))} e^{(\Gamma_v + \Gamma_c)t''/\hbar} \left. \right]
\end{aligned} \tag{36}$$

$$\begin{aligned}
& = 2\Re \left[|\langle v|P|c \rangle|^2 \frac{eE_0 e^{-i\omega t}}{2m\omega} \frac{1}{(E_c - E_v - \hbar\omega + i(\Gamma_c + \Gamma_v))} \right. \\
& + |\langle v|P|c \rangle|^4 \left(\frac{eE_0 e^{-i\omega t}}{2m\omega} \right)^3 \frac{1}{(E_c - E_v - 3\hbar\omega + i3(\Gamma_c + \Gamma_v))} \left(\frac{1}{2\omega} \right) \\
& \times \frac{1}{(E_c - E_v - \hbar\omega + i(\Gamma_c + \Gamma_v))} e^{2(\Gamma_c + \Gamma_v)t/\hbar} \left. \right]
\end{aligned} \tag{37}$$

The first term of the final result is the linear χ which goes into the index of refraction, and the second term is proportional to E^3 , i.e. it gives $\chi^{(3)}$. Here we have deduced only a frequency-tripling nonlinear effect with an ingoing and outgoing resonance, because we assumed only one input frequency. Of course, if we had written $A(t) = A_1(e^{i\omega_1 t} + e^{-i\omega_1 t}) + A_2(e^{i\omega_2 t} + e^{-i\omega_2 t}) + A_3(e^{i\omega_3 t} + e^{-i\omega_3 t})$ instead of $A(t) = A_0 e^{-i\omega t}$ as we did, then we would get all the frequency mixing terms associated with third-order optics, e.g. four-wave mixing (FWM).

As seen in (35), the prefactor $e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar}$ in each of the terms is exactly canceled out by a term with opposite sign in the exponent from the time integrals, so that the oscillation of the polarization is only at the driving frequency and the third-order harmonics.

Suppose that instead of continuing on forever, the electric field is shut off at $t = 0$, i.e.

$$A(t) = \begin{cases} A_0 e^{-i\omega t}, & t < 0 \\ 0, & t > 0 \end{cases} \quad (38)$$

Then for times $t > 0$, the integrals in (35) are time-independent. The only time dependence in $P(t)$ comes from the $e^{i(E_v - E_c)t/\hbar} e^{-(\Gamma_v + \Gamma_c)t/\hbar}$ prefactor. The polarization continues to oscillate at frequency $(E_v - E_c)/\hbar$, which is resonant at both ω and 3ω (the sum frequency). If there is no scattering (damping) it will continue ringing forever. The imaginary part of the self energy gives the rate at which the phase-coherent polarization dies. This is why it can be called a “dephasing” rate. There is also the feature, seen in (37), that the polarization grows exponentially in time at twice the decay rate, which implies the counterintuitive prediction that a FWM signal will have a longer rise time if there is less dephasing. This has been seen experimentally [9, 10].

In the case of delayed FWM, a third, “probe” wave follows two “pump” waves by some time delay. The strength of the fourth wave then gives a measure of the T_2 time. This is because the first two waves each create a polarization wave in the medium due to the *linear* term in (35), which decays according to the prefactor $e^{-(\Gamma_v + \Gamma_c)t/\hbar}$. These two waves then become contributions to E at later times, which mix with the probe wave via the third-order term. Since the strengths of the pump polarization waves decay, so will the delayed FWM signal, with exactly the same time constant.

We have seen then that the FWM dephasing rate and the line broadening are both controlled by the same imaginary self-energy, i.e. the T_2 time. This leads one to expect that the line width and the FWM dephasing rate should be inversely proportional. This is generally true, but can be incorrect when a continuum of states is excited, (e.g. by an ultrafast pulse with considerable Heisenberg energy uncertainty), which leads to interference between different oscillator frequencies, as seen in Ref. [11].

7 Scaling Laws in Recent Experiments

The electron-electron Coulomb scattering process represents a special case of the two-body scattering discussed in Section 4, because the interaction cross section diverges in the case of zero momentum transfer, and this divergence must be removed self-consistently by a screening length which depends on the density and the instantaneous energy distribution of the electrons. A previous publication [5] presented the results of scaling laws for electron-electron scattering based on a Boltzmann integral calculation taking into account the dependence of the self-consistent screening length on the density, using a method valid both for nonequilibrium and equilibrium electron plasmas. The main conclusions of that work are reviewed here.

First, the proper integral for the electron-electron scattering depends on the type of experiment. There are three different integrals which relate to the experiments. The first is the “total” scattering rate, i.e. the imaginary self-energy calculated in (20) above. This integral determines the rate of decay of $\chi^{(3)}$, as shown

	dephasing (T_2)	energy relaxation (T_1)
low density:		
3d	constant [12]	$n^{1/2}$ [2, 15, 16]
2d	constant	n [17]
high density:		
3d	$n^{1/3}$ [13]	$n^{2/3}$
2d	$n^{1/2}$ [14]	n [17]

Table 1: Density dependence of rates for electron-electron scattering predicted in Ref. [5]. Experimental confirmations are given in the references in the table.

above. A second integral is given by (15) weighted by the momentum exchanged by the electrons in a given scattering event. This typically controls the electron scattering rate determined in transport measurements. A third integral is given by (15) weighted by the energy exchanged by the electrons in a given scattering event. This determines the evolution of the carrier distribution function, which is typically recorded in time-resolved luminescence experiments. These three rates are approximately the same for hard-sphere scattering but are very different for Coulomb scattering. This means that the “relaxation time approximation,” in which all scattering processes are assumed to be characterized by a single “relaxation time,” is justified in the case of short-range interactions but breaks down completely for long-range Coulomb scattering.

Second, the scaling laws as a function of temperature and density for these various integrals were determined for both two dimensions and three dimensions. At that time, several experiments had been done which gave scaling laws consistent with the results of the calculations; recent experiments also fulfill the predictions of that theory. Table 1 gives a summary of the predicted density dependences and the experiments which have observed them. An important result is that this theory predicts that the dephasing rate is independent of density at low density, in basic agreement with recent experiments (Ref. [12]; also seen indirectly in Ref. [18].) The “high-density regime” is defined as the regime in which the classical screening length becomes comparable to the interparticle spacing. A full treatment of the scattering rate in this regime would require accounting for the quantum wavefunctions; however, the proper scaling law for the dephasing can be found by the simple assumption that the screening length is pinned at the interparticle spacing. This assumption also correctly gives the crossover from the high-density to low-density scaling regimes.

A third main conclusion of Ref. [5] was that the screening length of the electrons scales with density in same way even for a highly nonequilibrium distribution. Quantum memory effects are important in determining the exact evolution of polarization, but the scaling laws should remain the same even when quantum memory effects are taken into account.

Recent experiments showing a near-constant dephasing rate at low density have been interpreted in terms of optical phonon scattering [12]. A full study of dephasing as a function of the excitation photon energy and the temperature should distinguish between these two interpretations, since Ref. [5] also gave predictions for the temperature dependence of the scaling laws.

8 Conclusions

The isotropic quantum Boltzmann equation has been used to produce quantitative predictions for numerous experimental systems far from equilibrium [2, 3, 4, 5]. These calculations show that the integrals which enter

into these calculations are the same as the integrals which are used for optical line broadening and four-wave mixing, for the cases of a Fermi or nondegenerate Bose gas. In the case of electron Coulomb scattering, great care must be taken to use the properly weighted integral for different experiments.

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